

SILICON NITRIDATION AT DIFFERENT NITROGEN PRESSURES¹

E. B. Bendovskii²

Translated from *Steklo i Keramika*, No. 10, pp. 6 – 11, October, 2012.

The mass change of silicon samples with different initial density, apparent density, ultimate strength and phase composition during nitridation in the nitrogen pressure range 0.002 – 18 MPa is followed. It is shown that rate of the reaction of nitrogen and silicon increases up to nitrogen pressure 1.5 MPa; at higher nitrogen pressures the growth of the reaction rate slows down. Ceramic with relative density 90% and ultimate bending strength 540 MPa was obtained at kilning temperature 1710°C. Ceramic parts serviceable under the actual operating conditions of a real motor have been fabricated for internal combustion engines.

Key words: silicon nitride, reactive sintering, nitrogen pressure

There are a large number of works dedicated to the interaction of silicon with nitrogen. The experiments attest that impurities present in the reagents, the concentration of these impurities, the graininess of the initial silicon, the packing density of the silicon grains in the fabricated part and much else influence the mechanism and results of nitridation. The packing density of grains in silicon is of special interest because a ceramic can be obtained from reaction-sintered silicon nitride during nitridation of a part made from powdered silicon. Here, much less attention is given to the effect of nitrogen pressure on the flow of the nitrogen – silicon reaction than to the packing density of the ceramic grains and its effect on the flow of the silicon – nitrogen reaction.

The present work is devoted to some aspects of the effect of nitrogen pressure on the nitrogen – silicon interaction.

Grade KR-0 silicon (GOST 2169–69) with grain size less than 1.5 μm and pure grade nitrogen gas were used in this work.

The parts were formed by hot casting of a thermoplastic slip of silicon powder. Nitridation and heat-treatment of the parts in nitrogen were conducted in a wide range of the nitrogen gas pressures in a specially designed and fabricated setup [1].

The density of the silicon parts, nitridation temperature and time and the nitrogen pressure in the furnace were varied in the experiments.

The apparent density was determined on the parts formed. After nitridation the change of mass, linear shrink-

age, apparent density, ultimate bending strength and phase composition of the material were determined.

During nitridation kilning the temperature was measured inside the furnace and in the bulk of the silicon sample. The experimental results were processed by the least-squares method with confidence probability 90%.

NITRIDATION TEMPERATURE CURVES

The nitridation temperature curves obtained at different nitrogen temperatures are of the same form. The temperature changes in the furnace 1 and at the center of the silicon part 2 with heating with nitrogen pressure in the furnace 4 MPa are presented in Fig. 1.

To furnace temperature 1050°C the temperature at the center of the part is much lower than in the furnace. Starting at 1050°C the temperature at the center of the part becomes higher than in inside the furnace.

For furnace temperature above 1250°C the temperature at the center of the part increases sharply, reaching 1480°C.

Subsequently, in time the temperature at the center part becomes equal to the temperature inside the furnace.

It is obvious that starting at temperature 1050°C the flow of the exothermal reaction of silicon with nitrogen becomes noticeable: the part starts to heat up as a result of heat release.

At 1250°C the formation rate of silicon nitride becomes so high that there is not enough time for the heat to dissipate from the interior of the sample and the temperature there rises rapidly, surpassing the melting temperature of silicon (1410°C) [2].

¹ This work was performed under the direction of Doctor of Technical Sciences, Professor Iosif Yakovlevich Guzman.

² D. I. Mendeleev Russian Chemical Technology University, Moscow, Russia (e-mail: Bendovskii.E.B@yandex.ru).

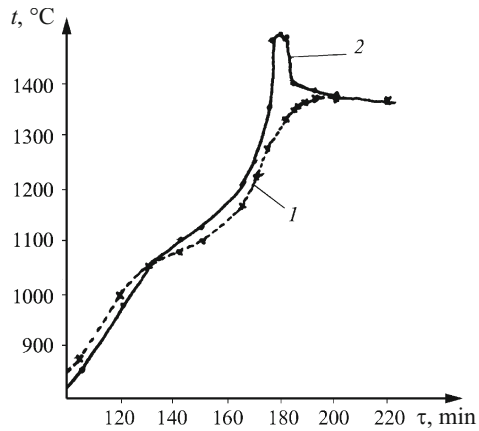


Fig. 1. Temperature change as a function of the nitridation time in the furnace (1) and at the center of the sample (2).

The unreacted silicon melts and large drops of melt form. The surface on which the heterogeneous nitrogen – silicon reaction occurs shrinks, the formation rate of silicon nitride decreases and less heat is released. Thus, in time the interior temperature of the part becomes equal to the temperature inside the furnace.

Silicon melt on the surface as well as rounded congealed drops in the interior are observed in parts nitrided at temperatures above 1250°C.

The temperature inside the furnace in which the temperature in the bulk of the part rises sharply depends noticeably on the nitrogen pressure inside the furnace (Table 1). Thus, at nitrogen pressure 0.002 MPa the sharp increase of the temperature in the interior of the part is observed at furnace temperature 1380°C. As the nitrogen pressure in the furnace increases to 4 MPa the temperature at the sharp increase (TSI) in the part decreases to 1250°C.

As nitrogen pressure continues to increase the TSI remains practically unchanged.

Since to nitrogen pressure in the furnace 4 MPa the TSI decreases with increasing nitrogen pressure it can be supposed that the determining factor in the formation rate of silicon nitride in the nitrogen pressure range 0.002 – 4 MPa is the nitrogen concentration in region where the direct nitrogen – silicon reaction occurs, i.e., the reaction proceeds in the diffusion region.

At nitrogen pressure 4 or more MPa the TSI remains constant, which can be an indication that the reaction has moved into the kinetic region.

NITRIDATION OF SILICON PARTS WITH DIFFERENT DENSITY

The results of nitridation of silicon parts with different initial density are presented Table 1 as a function of the nitridation time and nitrogen pressure.

The mass increase of the parts depends on their initial density at all nitrogen pressures.

TABLE 1. Relation between the Temperature and Nitrogen Pressure in the Furnace at TSI

Parameter	Nitrogen pressure in the furnace, MPa						
	0.002	0.1	0.3	1.0	4.0	13.0	18.0
Furnace temperature, °C	1380	1350	1320	1310	1250	1240	1240

TABLE 2. Nitridation of Silicon Parts at Temperature 1250°C

Initial part density ρ_{part} , g/cm ³	Nitrogen pressure in the furnace, MPa	Mass change of a part with nitridation $\Delta m/m$, %, over time	
		60 min	180 min
1.46	0.3	37.2	39.7
1.52		36.4	39.2
1.46	13	53.4	55.4
1.52		53.0	55.1

As the nitrogen pressure in the furnace increases from 0.3 to 13 MPa, the mass of the parts increases very noticeably: for nitriding time 60 min the mass increments are 36 and 53%, respectively. The appreciable dependence of the mass increase of the parts on the nitrogen pressure suggests that in this case the reaction proceeds in the diffusion region to nitrogen pressure 13 MPa.

Most of the silicon nitride is formed at the initial stage of the reaction — during the first 60 min. Increasing the nitridation time increases the mass increment by only 2 – 3% with nitridation time increasing from 60 to 180 min.

The applicability of the equation of [3] expressing the relation between the initial density ρ_{part} , the final density ρ_{nit} of a part after nitridation, and the mass increment $\Delta m/m$ of the parts at different nitrogen pressures was checked on samples with different initial density:

$$\rho_{\text{nit}} = \rho_{\text{part}} (1 + \Delta m/m).$$

The computed and experimental data obtained with nitridation at 1250°C for 180 min are presented in Table 3.

The experimental and computed density values agree well in the entire nitrogen pressure range.

The curves of the mass increase and ultimate bending stress as a function of the nitrogen pressure, which are presented in Fig. 2, are sigmoidal.

As mentioned above, the mass growth of parts at all values of the nitrogen pressure depends only weakly on the initial density of the parts at all nitrogen pressures. The largest increase of part mass occurs as nitrogen pressure increases to 1.5 MPa. No appreciable mass increase occurs for high nitrogen pressures.

In contrast to an increase of the mass of the parts the ultimate strength of nitrided parts depends appreciably on their

TABLE 3. Results of Nitridation of Samples at 1250°C for 180 min

Nitrogen pressure in the furnace, MPa	ρ_{part} , g/cm ³	$\Delta m/m$, %	ρ_{nit} , g/cm ³		α/β^*
			experimental	computed	
0.3	1.46	39.7	2.03	2.04	2.88
	1.52	39.2	2.10	2.12	
1.5	1.46	46.9	2.15	2.14	3.95
	1.52	46.7	2.24	2.23	
2.5	1.46	48.1	2.17	2.16	4.05
	1.52	47.9	2.26	2.25	
5.0	1.46	49.1	2.18	2.18	4.05
	1.52	48.8	2.27	2.26	
13.0	1.46	55.4	2.26	2.27	0.3
	1.52	55.1	2.35	2.36	
18.0	1.46	54.5	2.27	2.27	0.2
	1.52	54.1	2.35	2.35	

* The ratio of α and β of the Si_3N_4 phases.

initial density. Thus, the mass of parts with the initial densities 1.46 and 1.62 g/cm³ increases at nitrogen pressure 13 MPa by 53.8 and 53.0%, respectively. The ultimate bending strengths of the same parts are 245 and 276 MPa, respectively.

The largest increase of the strength of parts occurs with nitrogen pressure increasing to 5 MPa. At high nitrogen pressures the increase of strength slows down appreciably (see Fig. 2).

The increase of the ultimate strength of nitrided parts with increasing initial density of the parts is logical. However, the difference of the nitrogen pressures at which the curves of increasing increment and ultimate strength become almost parallel to the abscissa indicates the existence of other factors that affect the properties of the material. Of primary interest here is the existence of silicon nitride in the form of two polymorphous modifications.

A possible reason for the decrease of the strength of nitride parts at a polymorphic transition $\alpha - \beta$ Si_3N_4 is described in [4].

In this connection the change of the phase composition of the silicon nitride formed was followed as a function of the nitridation conditions — the density of the parts and the nitrogen pressure in the furnace.

The phase composition of the silicon nitride formed under the nitridation conditions used does not depend on the initial density of the parts (see Table 3).

The α -silicon nitride content increases from $\alpha/\beta = 2.88$ to $\alpha/\beta = 4.05$ as the nitrogen pressure in the furnace increases from 0.3 to 5.0 MPa, respectively.

As nitrogen pressure continues to increase the α -silicon nitride content decreases. At nitrogen pressure 13 MPa and

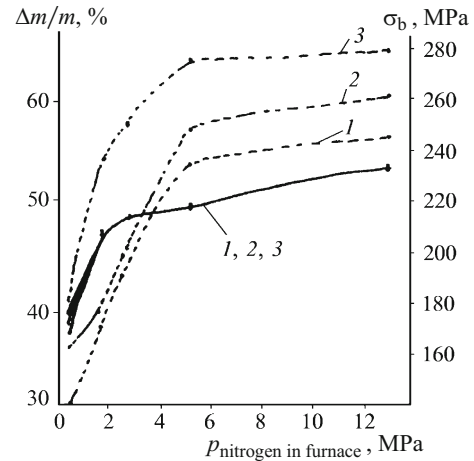


Fig. 2. Mass change (continuous curves) and ultimate strength (dashed curves) of nitrided samples versus the nitrogen pressure in the furnace: 1) $\rho_{\text{part}} = 1.46$ g/cm³; 2) $\rho_{\text{part}} = 1.58$ g/cm³; 3) $\rho_{\text{part}} = 1.62$ g/cm³; $t = 1250^\circ\text{C}$; $\tau = 180$ min.

higher the ratio α/β takes the values $\alpha/\beta = 0.3$ and lower (Table 3).

The sharp slowing of the growth in the change of the ultimate strength is due to the sharp change of the phase composition of the silicon nitride formed.

It could be that silicon nitride forms in the α -modification to nitrogen pressure 5 MPa. Two variants are possible at high nitrogen pressures:

- 1) crystallization of silicon nitride in the form of the α -modification and a higher rate of the polymorphous transformation;
- 2) crystallization of silicon nitride immediately in the β -modification.

At the same time an explicit dependence of the ultimate strength on the phase composition is not seen. Most likely, the particulars of the crystallization of silicon nitride, growth of its crystals and formation of the structure of a crystal body have a determining effect on the ultimate strength.

NITRIDATION OF SILICON PARTS AT HIGH TEMPERATURES

Nitridation of silicon parts at 1250°C makes it possible to obtain a mass increment no larger than 55% even at nitrogen pressure 18 MPa. In other words, up to 12% free silicon remains in the bulk of a part.

An efficient method of increasing the degree of transformation of silicon into nitride is to introduce a second nitridation step performed at a temperature above the melting temperature of silicon — 1410°C.

In this part of the work the nitridation of parts was conducted in the following regime:

first step — temperature 1250°C; nitrogen pressure in the furnace 1.5 MPa; time 180 min;

second step — temperature 1450 or 1710°C; nitrogen pressure in the furnace 5 MPa; time 60 min.

The nitrogen pressure in the furnace at the first step, equal to 1.5 MPa, is chosen on the basis of the fact that the mass increment of the parts starts to increase rapidly at this pressure (see Fig. 2).

The nitrogen pressure 5 MPa in the furnace at the second step is chosen because starting at this pressure the curves of the ultimate bending strength of the samples do not rise sharply (see Fig. 2).

The following determined the choice of the temperature at the second step:

a) 1450°C — certainly not by much but still higher than the melting temperature of silicon;

b) 1710°C — much higher than the melting temperature of silicon, and likewise determined by the technical capabilities of the equipment.

The results of nitridation of silicon parts with different density by the two-step regime are presented in Fig. 3.

The second — high-temperature — nitridation step increases the mass increment of the parts appreciably. The increment reaches 55.0 and 62.0% at 1450 and 1710°C (see Fig. 3), respectively. As in one-step nitridation the mass increment is largely independent of the initial density of the parts.

The ultimate strength of parts nitrided in the two-step regime appreciably increases with increasing part density. For the final nitridation temperature 1710°C the ultimate strength depends on the density of the parts more strongly than for temperature 1450°C and reaches 360 MPa at apparent density of the nitrided parts 2.62 g/cm³ ($\rho_{\text{rel}} = 82\%$). The inclusion of the second (high-temperature) step in nitridation led to shrinkage of the parts, amounting to about 1 and 1.5% at 1450 and 1710°C, respectively.

The phase composition of silicon nitride in the parts nitrided in the two-step regime is represented mostly in β -silicon nitride, whose amount in all cases reaches 95% of the total.

The existence of shrinkage, the presence of silicon nitride in the form of the β -modification and the increasing ultimate strength of nitride parts requires a study of the growth of the silicon nitride crystals formed and the formation of the structure of nitrided parts. This could be a subject of subsequent studies.

In summary, reactive sintering, during which a heterogeneous reaction of silicon with nitrogen occurs, gives ceramic samples consisting mainly of β -silicon nitride with density 2.62 g/cm³ ($\rho_{\text{rel}} = 82\%$) and ultimate bending strength 360 MPa.

NITRIDATION (HEAT-TREATMENT) OF SILICON PARTS CONTAINING YTTRIUM OXIDE

Reactive sintering of silicon parts makes it possible to obtain ceramic with relative density to 82%. At present it is

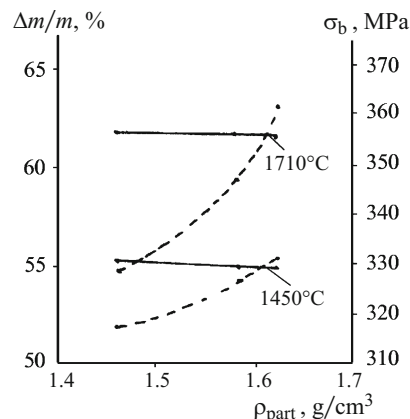


Fig. 3. Mass change (solid curves) and ultimate strength (dashed curves) of nitrided samples versus the apparent density of the samples in two-step nitridation: $t_1 = 1250^\circ\text{C}$; $p_{1\text{nitrogen}} = 1.5$ MPa; $t_1 = 180$ min; $t_2 = \text{var}$; $p_{2\text{nitrogen}} = 5.0$ MPa; $t_2 = 60$ min.

difficult to produce ceramic samples and pieces from high-density silicon nitride by reactive sintering. For this reason sintering additives with different composition, usually oxides of different metals — calcium, yttrium, are introduced into the initial batch.

In the present work yttrium oxide in the amount 2% (mass fraction) was introduced as the sintering additive. Yttrium oxide was introduced at the stage of preparation of the silicon powder. The parts were prepared in the same manner as from pure silicon.

The following regime was used for heat-treatment:

first step — temperature 1250°C; nitrogen pressure in the furnace 1.5 MPa; time 180 min;

second step — temperature 1450, 1510, 1680 and 1719°C; nitrogen pressure in the furnace 5 MPa; time 60 min.

At the second step heat-treatment was combined with the silicon nitridation completion process with sintering (densification), which yttrium oxide made possible.

The properties of the parts obtained are presented in Figs. 4 and 5.

It is obvious that the mass change of the parts, just as in parts containing no yttrium oxide, depends little on the initial density of the parts and reaches 62% at 1710°C (Fig. 4a), which is close to the theoretical value of the increment. At the same time it should be noted that this is a result of nitridation over the entire exposure time, but the mass change of the parts as a result of temperature variation was not followed in the present experiment.

Very appreciable shrinkage, which increases with the heat-temperature at the second step, is observed for the heat-treated parts (see Fig. 4). In addition, the shrinkage increases linearly with increasing apparent density of the parts in the experimental temperature range.

For initial apparent density of the parts 1.62 g/cm³ and temperature at the second heat-treatment step 1710°C the apparent density of the parts reaches 2.88 g/cm³ ($\rho_{\text{rel}} = 90\%$).

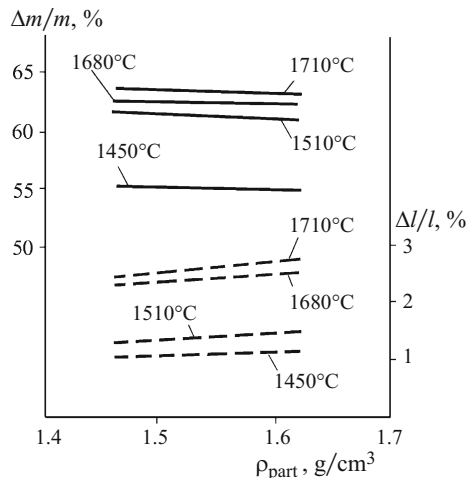


Fig. 4. Mass change (solid curves) and ultimate strength (dashed curves) of the samples containing yttrium oxide versus the apparent density of the samples in two-step nitridation: $t_1 = 1250^\circ\text{C}$; $p_{1\text{nitrogen}} = 1.5 \text{ MPa}$; $t_1 = 180 \text{ min}$; $t_2 = \text{var}$; $p_{2\text{nitrogen}} = 5.0 \text{ MPa}$; $t_2 = 60 \text{ min}$.

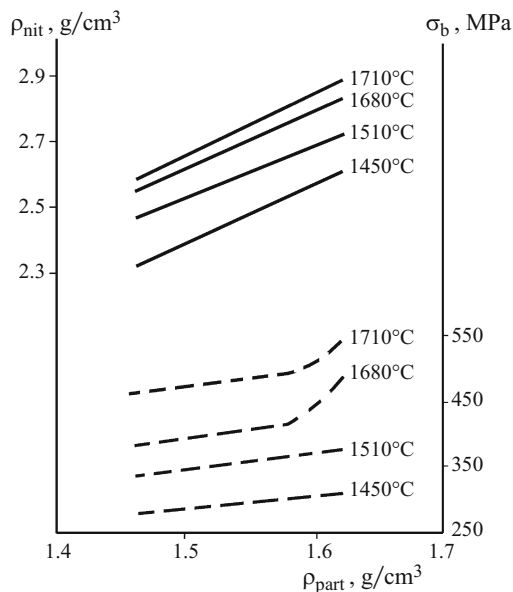


Fig. 5. Apparent density (solid curves) and ultimate strength (dashed curves) of the samples containing yttrium oxide versus the apparent density of the samples in two-step nitridation: $t_1 = 1250^\circ\text{C}$; $p_{1\text{nitrogen}} = 1.5 \text{ MPa}$; $t_1 = 180 \text{ min}$; $t_2 = \text{var}$; $p_{2\text{nitrogen}} = 5.0 \text{ MPa}$; $t_2 = 60 \text{ min}$.

It should be noted once again that two processes occur at this stage of heat-treatment:

- first — chemical reaction of nitrogen with silicon (mass increment);
- second — mass transport of the silicon nitride formed (shrinkage).

It is still unclear how these two processes proceed and how they combine and affect one another.

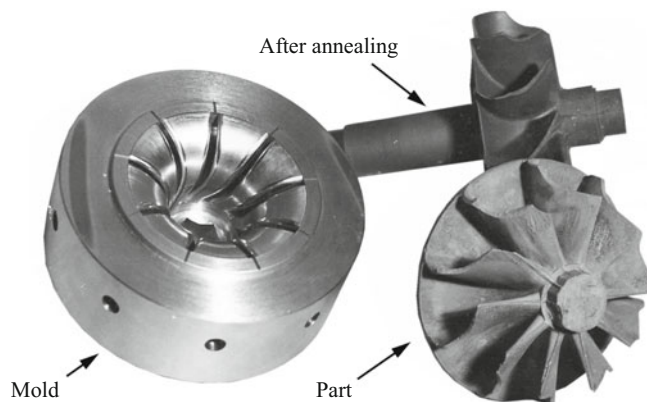


Fig. 6. Working wheel for a turbocompressor.

The ultimate bending strength of the parts heat-treated at 1450 and 1510°C increases monotonically with increasing apparent density of the parts (see Fig. 5). At heat-treatment temperatures 1680 and 1710°C the ultimate strength increases sharply at apparent density of the parts 1.62 g/cm³, reaching 540 at 1710°C (see Fig. 5).

The phase composition of the silicon nitride in heat-treated parts changes with increasing temperature toward enrichment with β -silicon nitride. So, x-ray phase analysis performed after heat-treatment at 1710°C showed the presence of silicon nitride only in the β -modification form.

As the final part of the work at this step but not the work as a whole, the results obtained were used to prepare parts of different shape: pistons for internal combustion engines (ICE) and working wheels for turbocompressors (Fig. 6).

After the fabricated parts were machined the working wheel for a turbocompressor was tested in the exhaust system of a KAMAZ engine. The tests showed that the turbocompressor wheel fabricated from silicon nitride is serviceable under real working conditions in an engine and reaches the working regime approximately two times faster than wheels fabricated from conventional materials.

CONCLUSIONS

Nitridation of silicon parts with different initial densities in the nitrogen pressure range 0.002 – 18 MPa was studied.

It was shown that the quantitative dependences of the apparent densities of the parts and nitrided samples and the mass change hold in the entire range of nitrogen pressures.

An increase of the nitrogen pressure to 1.5 MPa increases the formation rate of silicon nitride very noticeably. For high nitrogen pressures the reaction rate increases very little.

The formation rate of silicon nitride depends very little on the apparent density of the parts in the entire range of nitrogen pressures.

The ultimate bending strength of nitrided samples increases appreciably with nitrogen pressure increasing to 5.0 MPa and changes little at high nitrogen pressures.

The mass gain and ultimate strength change sharply at different nitrogen pressures: 1.5 and 5.0 MPa, respectively.

Ceramic samples with apparent density 2.88 g/cm³ ($\rho_{\text{rel}} = 90\%$) can be obtained by adding yttrium oxide into the initial silicon and introducing a second step for heat treatment at nitrogen pressure 5 MPa.

A series of parts, including a turbocompressor wheel, were fabricated from silicon nitride. The wheel proved to be serviceable under the conditions in a real engine.

REFERENCES

1. E. A. Anikin, V. I. Snop, I. Ya. Guzman, and E. B. Bendovskii, "Inventor's Certificate No. 1344516," *Byul. Izobr. Polez. Modeli*, No. 38 (1987).
2. R. A. Andrievskii and I. I. Spivak, *Silicon Nitride and Materials Based on It* [in Russian], Metallurgiya, Moscow (1984).
3. I. Ya. Guzman, *Reactive Sintering and Its Use in Ceramics and Refractories Technology, Teaching Notes* [in Russian], RKhTU im. D. I. Mendeleeva, Moscow (1996).
4. E. B. Bendovskii and I. Ya. Guzman, "Particulars of silicon nitridation," *Steklo Keram.*, No. 11, 22 – 26 (2003); E. B. Bendovskii and I. Ya. Guzman, "Specifics of silicon nitration," *Glass Ceram.*, **63**(11 – 12), 374 – 378 (2003).